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Geochemical assessment of the injection of CO_2 into Rousse depleted gas reservoir

Part II: geochemical impact of the CO_2 injection

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Abstract

45000 tones of CO_2 have been injected so far into the Rousse depleted gas reservoir, geological storage of the first French CCS operation.
Following a detailed mineralogical and thermodynamical characterization [1], this paper reviews the geochemical impacts of the CO_2 injection. Firstly, reactive pathways were identified, followed by a literature review of the reaction kinetics. Finally, a reactive transport model was set up.
This work confirms that Mano reservoir mineralogy and porosity are largely unaffected by the storage of CO_2. The major new finding is that the geochemical impacts are primarily dominated by pressure depletion rather than CO_2 acidity.

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CO_2 geological storage; Rousse; Geochemical modeling; Transport-reactive modeling

1. Introduction

TOTAL conducts the Lacq CO_2 pilot, the first French pilot to demonstrate the technical feasibility and reliability of an integrated CO_2 capture, transportation, injection and storage scheme from an oxy boiler [3].
The geological storage reservoir selected is the depleted Mano reservoir of Rousse field, a dolomitic

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reservoir at a depth around 4200 meters below sea level. The discovery well, Rousse-1, was drilled from August 1966 to June 1967 and discovered a gas accumulation with an initial pressure of 480 bars. It is the only well penetrating the Rousse Mano reservoir.

Gas production started in August 1972, initially from two reservoirs: Rousse Mano reservoir and deeper Rousse Meillon reservoir. Well penetration in the Meillon reservoir was plugged in May 1985 as a consequence of formation water arrival to the well. Production was restarted from Rousse Mano reservoir, and finally stopped in August 2008, with a flowing well pressure around 30 bars. Cumulative gas production from Rousse Mano reservoir is 910 MSm^3. The production well was then converted to an injection well.

CO_2 injection started in January 2010. 45000 tonnes of CO_2 have been injected so far, and current reservoir pressure is around 80 bar.

A preliminary geochemical study [2] has identified that chlorites contained within the reservoir rock could be dissolved as a consequence of CO_2 injection, and lead to the precipitation of new carbonates.

In order to confirm these findings, detailed mineralogical and thermodynamical assessments of the rock were conducted [1], leading to an update of the mineralogy of the reservoir rock, and more specifically to the confirmation of the presence of chlorite, but with a different composition.

From this updated minelogical compositon and thermodynamical model of the aqueous phase, the acido-basic geochemical impacts of the CO_2 injection were evaluated in three major steps:

- Firstly, reactive pathways were defined using CHESS, a geochemical software.
- A second step consisted in assessing reaction timescales, reviewing published data concerning both reactive surfaces and kinetic models of the identified minerals.
- Finally, a coupled geochemical – reservoir model was set up using GEM software, based on a history-matched reservoir model and a simplified geochemical model validated compared with the full Chess geochemical model. The validation included both the reactive pathways and kinetics. The 3D coupled model enables to locate the geochemical impacts, and to account for local pressure changes, which turn to be key in Rousse CO_2 storage case.

2. Initial geochemical model of the Mano reservoir rock

A first geochemical study was conducted in 2008 [2]. Mineralogy of the reservoir was assessed by combining XRD and XRF data, using a best fit approach. No direct measurement of the chemical composition of individual minerals was performed. This work concluded on a potential reactivity of chlorites identified from the best approach.

Following this study, an in-depth mineralogical study was performed, in order to verify the presence of the chlorite and to establish its chemical composition [1]. The study confirmed the presence of chlorite, and found that it is not a Fe-rich chlorite as believed previously but a Mg-rich chlorite, close to a Sudoite.

The following table summarizes the minerals identified, their chemical composition and their molar fraction. A thermodynamical equilibrium was reached with formation water and dissolved acid gases, for a pH of 4.9

Mineral	Composition	Molar fraction
Dolomite-ord	$CaMg(CO_3)_2$	89.77%
Calcite	$CaCO_3$	0.95%
Quartz	SiO_2	7.42%
Pyrite	FeS_2	0.53%
Apatite	$Ca_5F(PO_4)_3$	0.08%
Sudoite (Chlorite)	$(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$	0.05%
Muscovite	$(KAl_2)(Si_3Al)O_{10}(OH)_2$	0.35%
Montmor-Na	$(Al_{1.67}Na_{0.33}Mg_{0.33})Si_4O_{10}(OH)_2$	0.83%

3. Thermodynamical study of the acido-basic geochemical impact of CO_2

A first step of the study is conducted, looking at final thermodynamical equilibrium of the rock under an increasing partial pressure of CO_2 (in order to model the CO_2 geological storage process). Hence, kinetic processes are not modeled. Moreover, only acid-base reactions are modeled.
The objective is to identify reactive pathways resulting from the injection of CO_2, and consequences in term of petrophysics.
Chess batch geochemical software is used for this modeling step [3].

3.1. Dissolution of chlorite

A first reactive phase is modeled, where CO_2 injection leads to the dissolution of Chlorite, and subsequent mineral readjustments. For one mole of CO_2 injected, the balance equation is the following:

$$CO_2 + 6.04\ \text{Quartz} + 1.48\ \text{Calcite} + 0.93\ \text{Sudoite} + 0.72\ Na^+ \rightarrow 0.21\ CO_{2(aq)} + 1.14\ \text{Dolomite-ord} + 2.19\ \text{Montmor-Na} + 0.34\ Ca^{2+} + 0.03\ Mg^{2+} \quad (1)$$

The main mechanisms are

- A transfer of Aluminium and Silica from the Siderite to the Montmorillonite, Quartz providing the required amount of Silica
- A consumption of Na+ initially contained in the formation water
- A net consumption of 0.79 moles of CO_2 only, due to the precipitation of Dolomite
- A decrease of pH from 4.9 to 4.55 (note that equation 1 does not represent H^+ changes, as the amounts are very limited)

3.2. Reactive pathway in presence of Kaolinite and chlorite

During a second phase, after 0.36 molal of CO_2 was added to the system, Na+ lacks to allow the precipitation of Montmorillonite, Kaolinite becomes saturated, and it replaces Montmorillonite to consume the Al^{3+} produced by the dissolution of the Sudoite.
The geochemical reaction is described by equation 2:

$$CO_2 + 0.5\ \text{Quartz} + \text{Calcite} + 0.5\ \text{Sudoite} \rightarrow \text{Dolomite} + \text{Kaolinite} \quad (2)$$

This second reactive pathways occurs as long as Sudoite is available. pH is unchanged to the value of 4.55. This mechanism is similar to the one identified during the previous study [2], eventhough Siderite was precipitating instead of Dolomite, as the Chlorite was initially assumed to be Fe-rich.

3.3. Geochemical evolution after chlorite is fully dissolved

A third phase is predicted by the geochemical model. Once all Sudoite is dissolved, Dolomite continues to precipitate due to the availability of Ca^{2+} and Mg^{2+} (from equation 1) and incremental mass of CO_2 available in the system. The lack of Mg^{2+} in stoechiometric quantities leads to the dissolution of Montmorillonite. This mechanism tends to increase the pH despite the injection of CO_2. As quantities of H+ involved are limited compared to other compounds, it is not represented in this third phase:

$$CO_2 + 0.14\ \text{Calcite} + 0.46\ \text{Montmor-Na} \rightarrow 0.71\ CO_{2(aq)} + 0.15\ HCO_3^- + 0.14\ \text{Dolomite-ord} + 1.1\ \text{Quartz} + 0.37\ \text{Kaolinite} + 0.15\ Na^+ + 0.1\ Mg^{2+} \quad (3)$$

Note that for higher quantities of CO_2, Dawsonite would theoretically appear in the system. However it would correspond to a molality of $CO_{2(aq)}$ of 1.4 molal, and a pressure of CO_2 over 200 bar, that cannot be reached during the Rousse CO_2 geological storage.

3.4. Impact on mineralogy, porosity and pH

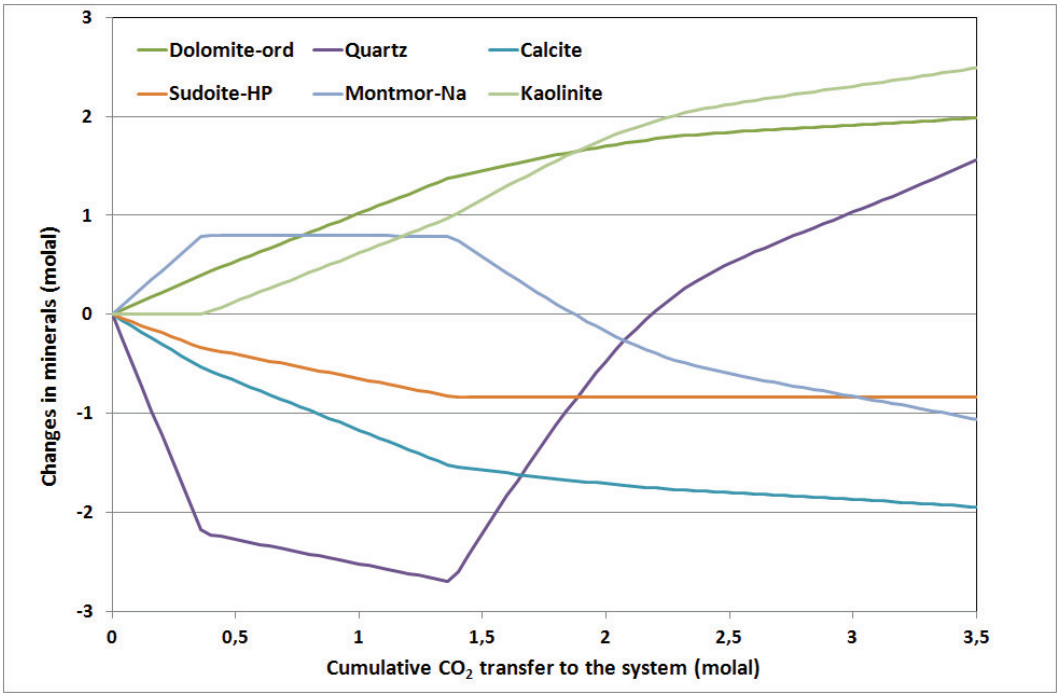

Fig. 1. Changes in mineralogy due to an input of CO_2 (molal). Sudoite (chlorite) is progressively dissolved. A net mineralization is obtained through the precipitation of Dolomite

The mineralogical impact of the three phases described above is summarized in figure 1.
From these reactive pathways, porosity remains largely unchanged, with a maximum absolute change of 0.03%. The trend is a slight decrease of porosity from an initial value of 3%, and a final value over 2.97%).
Impact of the CO_2 storage on the pH and the amount of aqueous CO_2 is presented on figure 2.

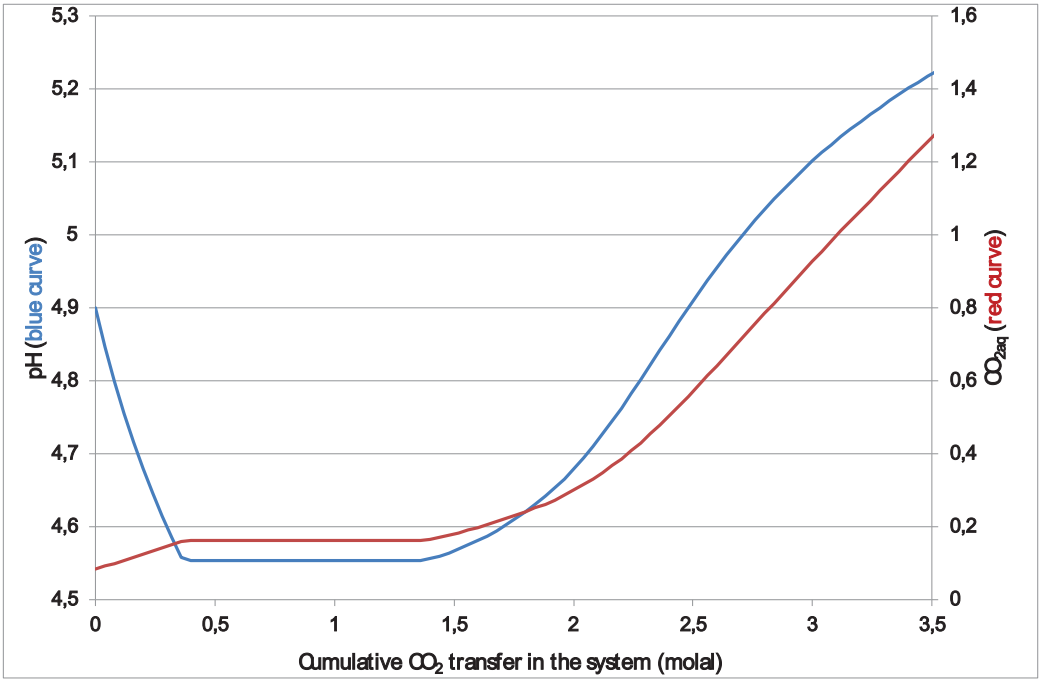

Fig. 2. Changes of pH and aqueous CO_2 as a consequence of the CO_2 storage process

3.5. Conclusion of the thermodynamical study and simplification of the geochemical model

From this phase of the work, it is concluded that minor changes are expected in porosity and pH. The main reactive pathway is the consequence of the dissolution of Sudoite (chlorite). This mineral is only a marginal mineral as the matrix consists primarily in an assemblage of Dolomite, Quartz and Calcite. As such the structure of the matrix is not expected to change as a consequence of CO2 injection/
This work also enables to highlight minerals that do not contribute to the reactive pathways:

- Muscovite, Pyrite and Apatite are largely unaffected by the reactions and can be removed (considered as non reactive) from the chemical system
- Considering these minerals as non reactive is indeed a significant simplification to the chemical system as it removes Fe, F, P and K from the list of elements to be considered for further chemical modeling.
- S element is not removed from the system, as H_2S is initially present and partially controls pH.
- Accounting for oxydo-reduction would require to reconsider this simplification, as Pyrite for example is potentially affected by oxidation processes, especially in the case of O_2 co-injected together with CO_2

4. Batch kinetic modeling

A second step of the study consists in defining the kinetic models of the identified reactions. It enables to evaluate the timeframe of the CO_2-induced reactions.

4.1. Literature review of the kinetic data relevant for Rousse CO_2 storage

Following the results of the previous section, kinetic models for the dissolution of Quartz, Calcite and Sudoite are required, as well as kinetic models for the precipitation of Montmorillonite, Dolomite and Kaolinite, which is the only neo-mineral of the system.
Kinetic model for Calcite dissolution is derived from Palandri & Kharaka [4]. This is the fastest reaction of the chemical system.
Following a review of publications on chlorite dissolution, the kinetic model for the Sudoite is the one studied by May et al [5] for a Clinochlore chlorite and interpreted by Naguy [6].
Kinetic model for Quartz is the one used in Palandri & Kharaka [4].
For Dolomite precipitation, the approach from Andre [7] is used.
For Kaolinite precipitation, interpretation of precipitation velocities by Xu et al are used [8]. These data are also used for Montmor-Na, due to the lack of data on the precipitation of this mineral.

4.2. Selection of reactive surfaces

Reactive surface is a key parameter of any kinetic model, and are very difficult to establish at reservoir conditions. Experimentally, the kinetic constant are calculated by dividing the apparent reaction velocities by a reactive surface, generally estimated either from Na-adsorption isotherms or from geometric calculations based on shape and size of mineral grains. Hence, we tend to consider kinetic constant of minerals as intrinsic ones, even though they are largely dependant on the structure of the samples and rocks being studied.
We have used reactive surfaces following the approach from Xh et at [8].
Concerning Kaolinite, the only neo-mineral of our system, it becomes oversaturated as a consequence of the accumulation of Silica and Aluminium in the aqueous phase. Precipitation of the mineral is initiated at nucleation points, defined as a surface per volume of solution.
Table below summarizes the kinetic parameters of each mineral at 150°C.

Mineral	Mechanism	R. Surface cm^2/g	LogKH+ (nH+)	LogKCO2 (nCO2)	LogKn
Dolomite-ord	Precipitation	9.8	-	-	-8.7
Calcite	Dissolution	9.8	0.445 (1)	0.528 (1)	-4.59
Quartz	Dissolution	9.8	-	-	-9.33
Sudoite	Dissolution	9.8	-7.95 (0.5)	-	0
Montmor-Na	Precipitation	151.6	-	-	-9.75
Kaolinite	Neo-mineral	151.6	-	-	-9.75

4.3. Expected time scales of the geochemical alterations using a batch model

A batch geochemical run is performed with the above mentioned kinetic models. It consists in replacing

the reservoir initial gas (at 480 bar) with a 100 bar stream composed of 95% CO_2 and other chemically inert gases. At this stage, the volume of gas is considered infinite compared to the volume of water, ie the fugacity of the various gas components is not modified from the chemical processes.

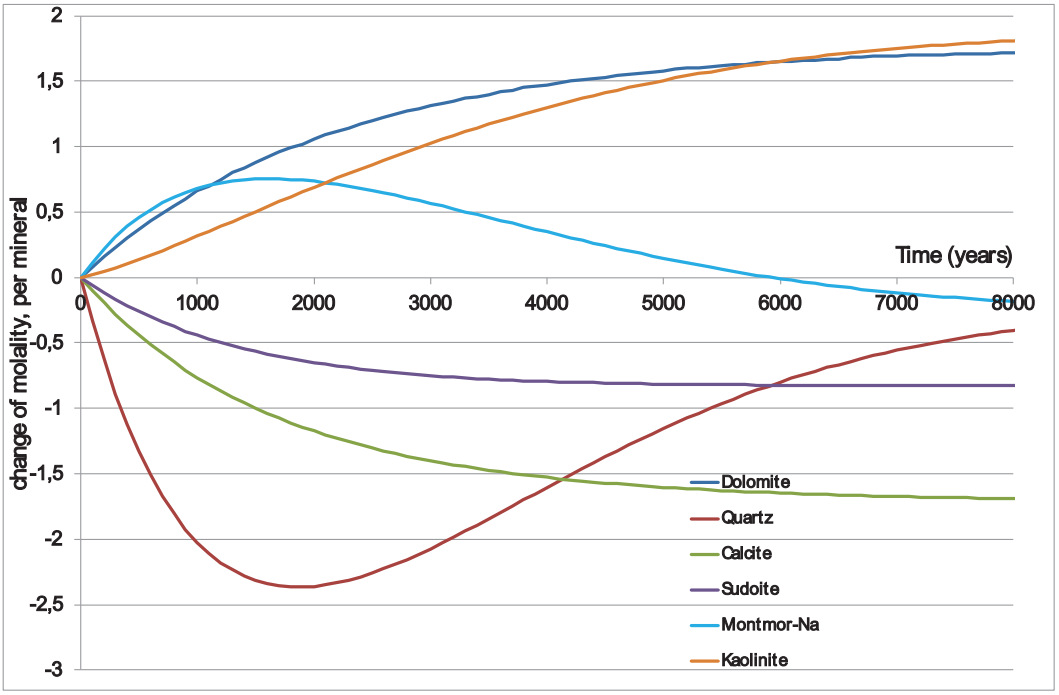

Fig. 3. Batch kinetic model of the Rousse Mano reactivity

The key findings of this batch, kinetic run is that the reactions are initiated smoothly, on a period over 100 years to become significant, and second phase of the reactivity is a very slow process (over millenniums) due to the slow precipitation of the Kaolinite, the new mineral of the system.

5. Reactive-transport modeling

The purpose of this work is to locate the CO_2 geochemical impacts and estimate the timing of the impacts, through the coupling the chemical effects and a multiphase, flow model. This is performed using GEM software [9].
As no significant impact on the porosity results from the various reactive pathways identified, no permeability changes are assumed as a consequence of the geochemical impacts.

5.1. Set up of a GEM reservoir transport model

To set up the GEM model, is to limit the chemical components (ions, aqueous species and minerals) to those involved in the reactive pathways in order to have an acceptable CPU run time. For example Ca-containing elements in the aqueous phase of the chemical batch model include Ca^{2+}, $CaCl^{+}$, $CaCl_{2(aq)}$, $CaHCO_3^{+}$, $CaCO_{3(aq)}$ and $CaOH^{+}$, however the chemical system can be limited to using Ca^{2+}.

Finally, the retained aqueous species are

- 9 basis aqueous species: $CO_{2(aq)}$, $H_2S_{(aq)}$, H^+, Ca^{2+}, Mg^{2+}, $SiO_{2(aq)}$, Na^+, Cl^-, AlO_2^- (Al-ion containing most of the Aluminium in the aqueous phase)
- 3 secondary species: OH^-, HCO_3^- and HS^-

The 6 minerals used during the batch kinetic modeling are of course included in the GEM model. Dissolution/precipitation reactions are re-written using the above mentioned aqueous species.

Kinetic models are also simplified, according to available models within GEM software. All catalytic terms (activation through CO_2 of Calcite and through pH of Sudoite) are removed, and kinetic constant are adjusted to match the initial full kinetic model:

- For Calcite: logk = -0.64. This value correspond to a pH between 4.5 and 5 with a partial pressure of CO_2 of 10 bar. As Calcite remains the mineral with the fastest reactivity, its kinetic reaction has a limited influence on the global chemical system, controlled by slower mechanisms
- For Sudoite: logk = -10.32. This value is obtained for a pH of 4.7. It is justified by the limited range of pH due to CO_2 injection (figure 2 above).

In order to ensure that these simplifications are not impacting the chemical system, a single cell GEM model using these simplifications is compared with the Chess results presented above.

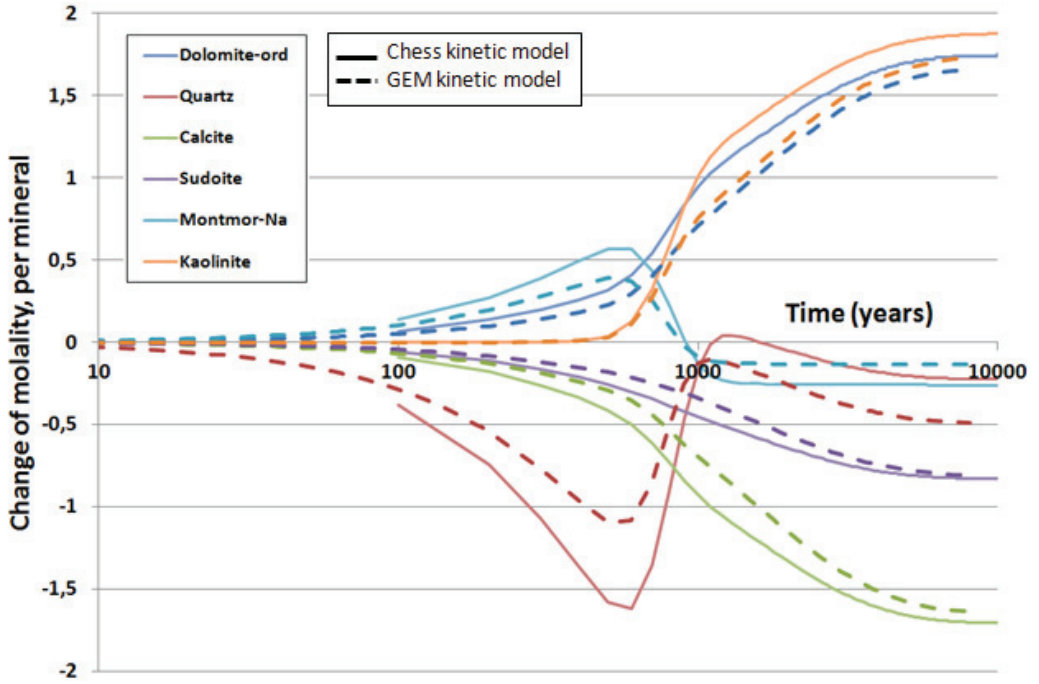

Fig. 4.Comparison of a single cell GEM model with a full Chess chemical model

This match is considered as satisfactory as both reaction amplitude (in term of molality change per mineral) and time scales are similar. Note that a similar match is obtained with pH and porosity (no significant change obtained in any model for porosity).

An Eclipse reservoir flow model of the Rousse gas reservoir was set up and history matched with historical production and pressure data in order to model the CO_2 injection [10]. This model was transferred from Eclipse to GEM format, using a similar gas and condensate Equation Of State representation with 18 components, including CO_2 and H_2S (H_2S impacting marginally the initial pH of the system).
A part from modeling CO_2 geochemical impacts, dedicated models were also used to model long term migration of CO_2 in the reservoir and water vaporization in the vicinity of the injector [10].

5.2. CO_2 impacts on mineralogy and porosity and pH

The following figure indicates te global change in term of moles per mineral in the Rousse reservoir.

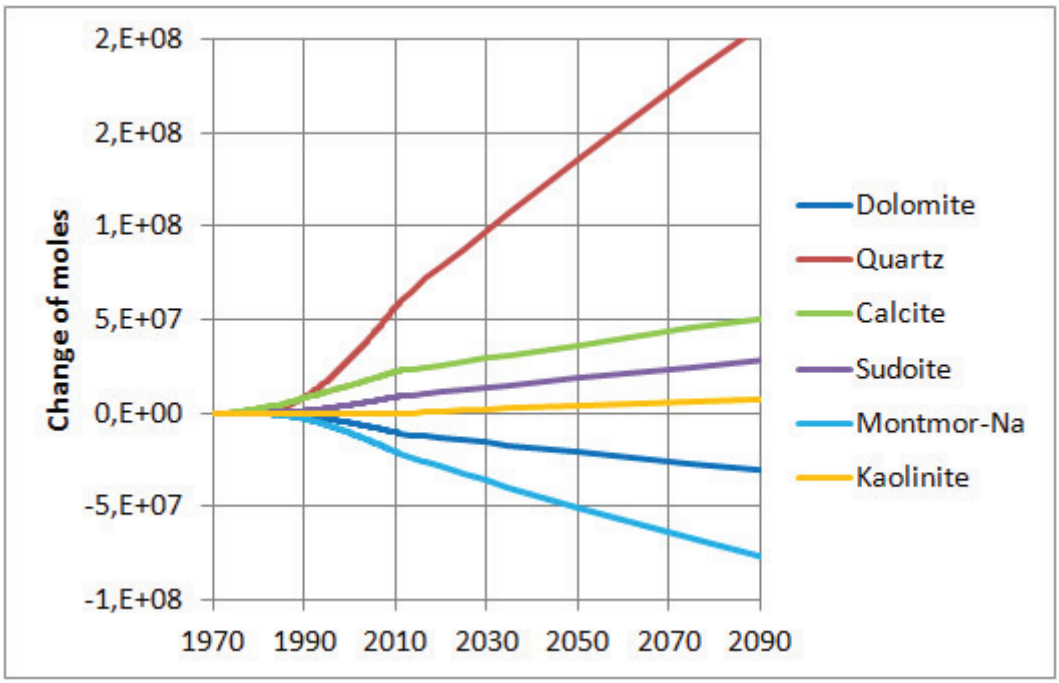

Fig. 5.Dissolution/precipitation of minerals within Rousse reservoir

One notes easily that the trend is opposite to the one given in figure 4. Also the chemical effects take place significantly earlier than the start of the CO_2 injection, in January 2010.
This opposite trend is explained by the on-going global pressure depletion taking place in the reservoir, due to a large depletion at the well and a progressive and regular depletion elsewhere.
In figure 6, a 3D view of the CO_2 injection is presented: the CO_2 is injected at the west-end (left of the figure) of the reservoir, leaving most of the gas reservoir unaffected by CO_2 injection. On the right part of the graph, a pH map is provided, showing a significant pH decrease around the injector but a global pH increase elsewhere. Note that initial pH in the model is 5.0. Time variations of pH is provided in figure 7 on two different locations: one near the CO_2 injector and another one away from the well.

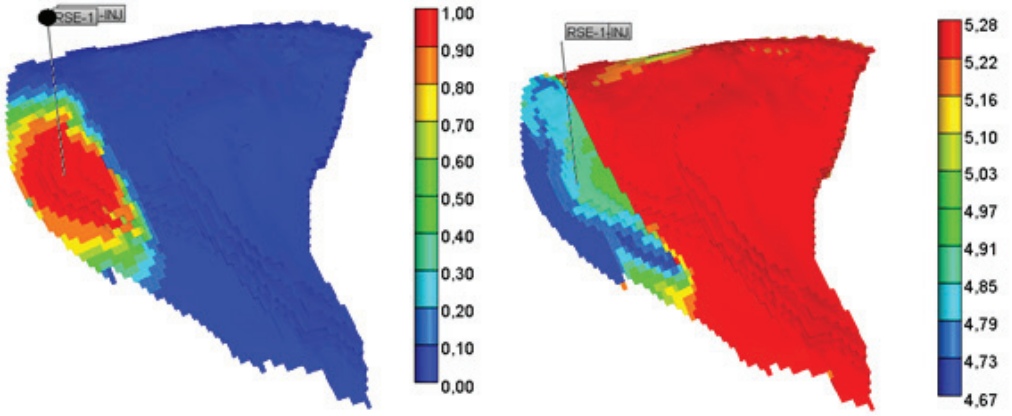

Fig. 6. 3D View of the reservoir and well location. Left: CO_2 fraction in the gas at the end of the CO_2 injection, right: pH in the reservoir formation water modeled in year 2100 (initial pH is 5.0)

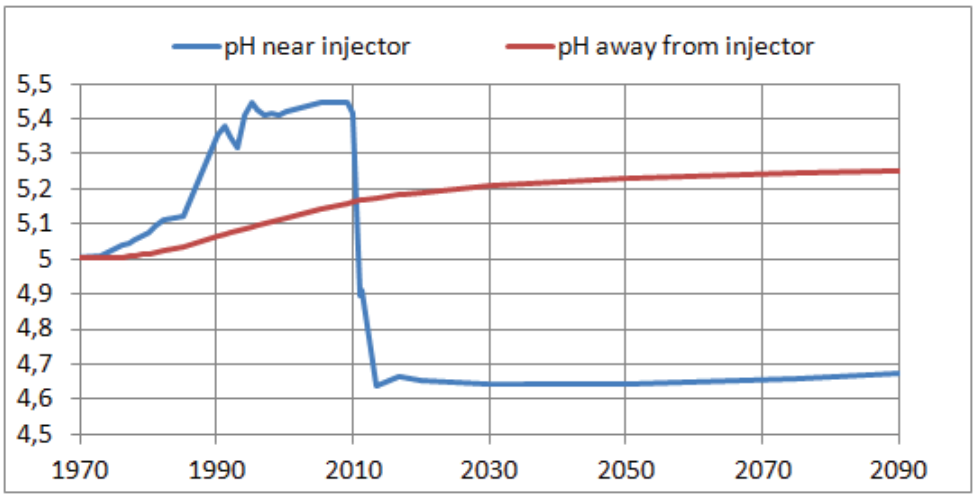

Fig 7: Variation of pH near injector and away from injector

Near the injector, pH raises initially significantly before the start of injection. Indeed, the large pressure decrease leads to degassing the formation water from any dissolved CO_2 and, hence, an increase of pH. This is followed, after injection start in 2010 by a rapid decrease of pH due to the CO_2 dissolution in the formation water. At a location far from the injector, there is no migration of injected CO_2, and the only ongoing process is the raise of pH due to the decrease of pressure.

This opposite behavior between CO_2 induced geochemistry (figure 3) and global reservoir trend (figure 5) is verified when plotting ongoing mineral precipitation and dissolution in the reservoir, on figure 8. The figure clearly indicates that the reactive pathway is opposite in the CO_2 injection area and away from injection area.

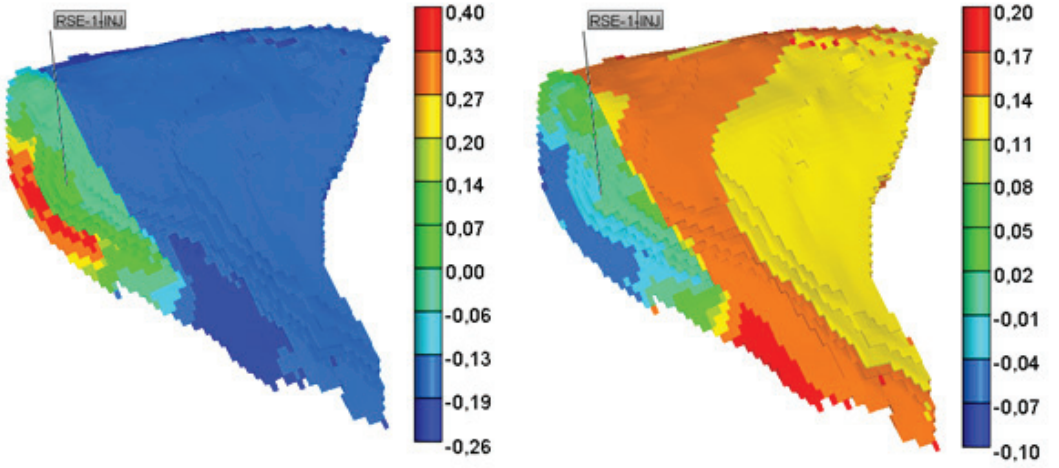

Fig 8: Changes in Dolomite (left) and Chlorite/Sudoite (right) in mol per m3 (positive is precipitation; negative is dissolution)

6. Conclusions

Key findings of this study are:

- The fact that a preliminary, quick look geochemical assessment was useful in order to identify critical minerals that could be investigated further with more details at a later stage
- The detailed study confirms the fact that porosity is expected to vary only marginally as a consequence of CO_2 injection. This result is particularly relevant as concerns where expressed on the chemical impact of CO_2 on carbonates
- As both the Mano reservoir mineralogy and porosity are largely unchanged after the CO_2 flooding, no consequences are expected on rock geomechanical properties
- The coupled geochemical-reservoir model enables to distinguish between geochemical effects due to the initial production of the reservoir and those due to CO_2 injection. Near the injector, the pre-injection depletion has the same pH impact (+/-0.5) as the CO_2 injection, but with the opposite sign. Away from the injection area, the chemical system is driven by pressure changes leading to a global pH increase in the field.

All these results underline the limited geochemical impacts of CO_2 in the reservoir.

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